

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-189647

(43)Date of publication of application : 13.07.1999

(51)Int.Cl.

C08G 65/28  
C08G 59/14  
G03G 9/087

(21)Application number : 10-180402

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(22)Date of filing : 26.06.1998

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(30)Priority

Priority number : 09292613

Priority date : 24.10.1997

Priority country : JP

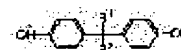
## (54) POLYOL RESIN AND ELECTROPHOTOGRAPHIC TONER

(57)Abstract:

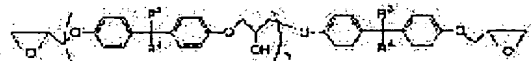
PROBLEM TO BE SOLVED: To obtain a polyol resin excellent in low-temp. fixability by reacting a bisphenol, a bisphenol epoxy resin, at least one compd. selected from among polyhydric alcohols and reaction products of polyhydric alcohols with acid anhydrides, and an active hydrogen compd.

SOLUTION: This polyol resin, having a number average mol.wt. of 1,000-10,000, a ratio of wt. average mol.wt. to number average mol.wt. of 5-50, a softening point of 85-150° C, and a glass transition temp. of 50-90° C, is obtd. by the polyaddition of a bisphenol

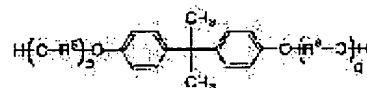
of formula I (e.g. bisphenol A), at least one bisphenol epoxy resin of formula II, at least one compd. selected from among polyhydric alcohols (e.g. an arom. diol of formula II) and reaction products of polyhydric alcohols with acid anhydrides, and an active hydrogen compd. in a specified ratio at 120-180° C in the presence of a catalyst. In the formulas, R1 to R4 are each H, methyl, or the like; R5 and R6 are each ethylene or propylene; (n) is 0 or higher; and (p) and (q) are each 1 or higher provided p+q is 2-10.



I



II



III

## LEGAL STATUS

[Date of request for examination]

15.08.2003

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's  
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[Date of extinction of right]

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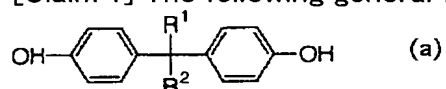
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**CLAIMS**

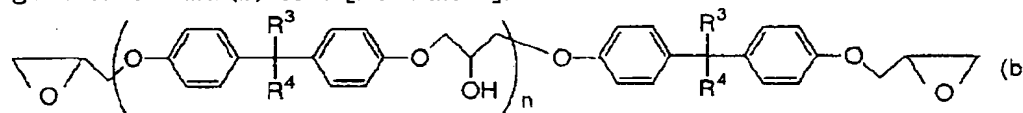

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[Claim(s)]

[Claim 1] The following general formula (a): [Formula 1]

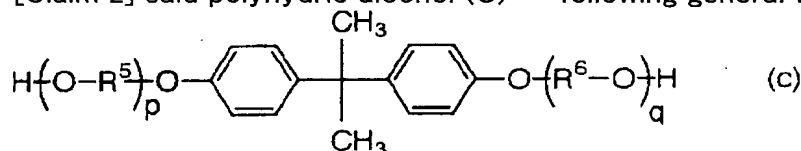


The bisphenols (A) expressed with (R1 and R2 being the same, or differing from each other, and being a hydrogen atom, a methyl group, an ethyl group, or a phenyl group), the following general formula (b): It is [Formula 2].



It is polyol resin to which make at least one sort chosen from the reactant (D) of the bisphenol mold epoxy resin (B) expressed with (R3 and R4 may be the same, or may differ, are a hydrogen atom, a methyl group, an ethyl group, or a phenyl group, and n is zero or more integers), and a polyhydric alcohol (C) and this polyhydric alcohol and an acid anhydride, and the compound (E) which has an epoxy group and at least one active hydrogen radical which reacts in intramolecular come to react.

[Claim 2] said polyhydric alcohol (C) — following general formula (c): — [Formula 3]



It is polyol resin according to claim 1 which is the alkylene oxide addition product of the dihydric phenol expressed with (R5 and R6 may be the same, or you may differ among a formula, are ethylene or a propylene radical, p and q are one or more integers, and p+q is 2-10).

[Claim 3] Polyol resin according to claim 1 whose ratio (Mw/Mn) of 1000-10000, and weight average molecular weight/number average molecular weight 50-90 degrees C and number average molecular weight (Mn) is [ softening temperature ] 5-50 for 85-150 degrees C and Tg.

[Claim 4] Polyol resin according to claim 1 said whose bisphenol mold epoxy resin (B) is the mixture of two or more sorts of bisphenol mold epoxy resins which have different number average molecular weight.

[Claim 5] Polyol resin according to claim 1 to 4 which performs said reaction using a cross linking agent (F) further.

[Claim 6] The aforementioned bisphenols (A), a bisphenol mold epoxy resin (B), The reactant of polyhydric alcohol (C), this polyhydric alcohol, and an acid anhydride (D), A compound (E) and a cross linking agent (F) The following formula : A: Weight N5of bisphenol A: The active hydrogen equivalent B1 of a bisphenol : Weight NB1 of a low-molecular-weight bisphenol mold epoxy resin : weight-per-epoxy-equivalent B-2 of a low-molecular-weight bisphenol mold epoxy resin : Weight-per-epoxy-equivalent C of the amount bisphenol mold epoxy resin of

weight NB2: giant molecules of the amount bisphenol mold epoxy resin of giant molecules :  
 [ The weight NC of polyhydric alcohol ] : Polyhydric-alcohol active hydrogen equivalent D:  
 The amount ND of the acid anhydride with which a reaction with polyhydric alcohol is  
 presented : Molecular weight E of an acid anhydride : amount NE of the compound which has  
 an epoxy group and one active hydrogen which reacts in intramolecular : Molecular weight F  
 of the compound which has an epoxy group and one active hydrogen which reacts in  
 intramolecular: Weight NF of a cross linking agent : The active hydrogen equivalent of a cross  
 linking agent, weight per epoxy equivalent (in the case of an acid anhydride, it is molecular  
 weight)

[Equation 1]

$$10000 \geq \frac{2(A + B_1 + B_2 + C + D + E + F)}{E/N_E + |E/N_E + A/N_A + C/N_C + F/N_F - B_1/N_{B_1} - B_2/N_{B_2}|} \geq 1000 \quad (1)$$

(1) は製造しようとする樹脂の理論分子量を表す。

$$1.2 \geq \frac{B_1/N_{B_1} + B_2/N_{B_2}}{E/N_E + A/N_A + C/N_C + F/N_F} \geq 0.85 \quad (2)$$

(2) はエポキシ基当量数と活性水素基当量数の比を表す。

$$0.4 \geq \frac{B_2}{A_1 + B_1 + B_2 + C + D + E + F} \geq 0 \quad (3)$$

(3) は全原料中の高分子量エポキシ樹脂の割合を表す。

$$0.4 \geq \frac{C + D}{A_1 + B_1 + B_2 + C + D + E + F} \geq 0.03 \quad (4)$$

(4) は全原料中の多価アルコールまたは多価アルコールと酸無水物との反応物の割合を表す。

$$D = N_D \times C/N_C \quad \text{または} \quad D = 0 \quad (5)$$

(5) は多価アルコールと酸無水物の量比を表す。D = 0 は多価アルコールのみで反応する場合を表す。

$$0.15 \geq \frac{F}{A_1 + B_1 + B_2 + C + D + E + F} \geq 0.001 \quad (6)$$

(6) は全原料中の架橋剤の割合を表す。

但し架橋剤が3官能以上のエポキシ樹脂の場合は(1)および(2)式は(7)および(8)式となる。

$$10000 \geq \frac{2(A_1 + B_1 + B_2 + C + D + E + F)}{E/N_E + |E/N_E + A/N_A + C/N_C + F/N_F - B_1/N_{B_1} - B_2/N_{B_2}|} \geq 1000 \quad (7)$$

$$1.2 \geq \frac{B_1/N_{B_1} + B_2/N_{B_2} + F/N_F}{E/N_E + A/N_A + D/N_D} \geq 0.85 \quad (8)$$

Polyol resin according to claim 1 to 5 made to come to react at a rate to satisfy.

[Claim 7] The toner for electrophotography which uses polyol resin according to claim 1 to 6 as a principal component.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] Especially this invention relates to polyol resin useful as a toner for dry developing which develops the electrostatic-charge image or the magnetic latent image in the electrophotography of a copying machine, facsimile, a printer, etc., and the toner for electrophotography which uses the polyol resin as a principal component about polyol resin and the toner for electrophotography.

[0002]

[Description of the Prior Art] In the electrophotography of a copying machine, facsimile, a printer, etc., there are a wet-developing method and a dry-developing method as an approach of developing an electrostatic-charge image, and a dry-developing method is used in many cases. By the dry-developing method, the frictional electrification developer which mixed carriers, such as iron powder and a glass bead, is used for the toner impalpable powder which made the resin for toners used as a binder contain coloring agents, such as carbon black, and other additives. The toner image obtained here is imprinted on sheets, such as a form, and it is the heat-and-pressure roller which has a mold-release characteristic to a toner after that, or in order to obtain a duplication, form an electrostatic latent image in a photo conductor, and the toner of frictional electrification nature is made to usually adhere to this electrostatic latent image electrically, and negatives are developed, and it considers [ you make it established by the flash plate light source, and ] as a permanent visible image. In the case of a magnetic latent image, after developing the latent image on a magnetic drum with the toner containing the magnetic substance, fixing is presented as mentioned above.

[0003] This kind of toner is required to excel in fixable (for a toner to adhere to a form firmly), and blocking resistance (for a toner particle not to condense). Furthermore, hot calender roll fixing requires offset-proof nature (a toner should adhere to a fixing roller and a form should not become dirty). Reduction of power consumption when a copying machine, facsimile, or a printer uses these devices in recent years as it spreads also through domestic, and improvement in visible image formation speed are required, and using binder resin with low fixing temperature is called for. In order to lower fixing temperature, generally approaches, such as lowering the softening temperature of binder resin and narrowing molecular weight distribution, are adopted. However, by these approaches, offset-proof nature and blocking resistance fall. For this reason, low-temperature fixing-ization of a toner is in the situation which cannot be referred to as still enough.

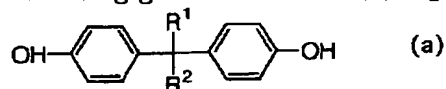
[0004]

[Problem(s) to be Solved by the Invention] Then, since the purpose of this invention solves the problem which the conventional toner has, and is excellent in low-temperature fixable one and excellent in offset-proof nature and blocking resistance, it is to offer polyol resin suitable as resin for toners, and the toner for electrophotography which uses the polyol resin as a principal component.

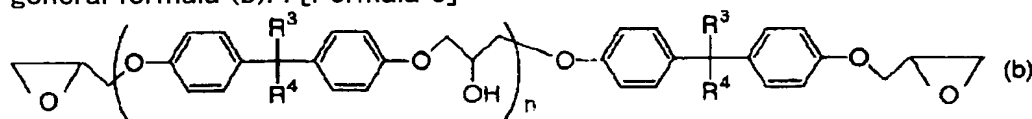
[0005]

[Means for Solving the Problem] In order to solve said technical problem, this invention is the

following general formula (a). : [Formula 4]



It is [ the bisphenols (A) expressed with (R1 and R2 being the same, or differing from each other, and being a hydrogen atom, a methyl group, an ethyl group, or a phenyl group), and ] the following general formula (b). : [Formula 5]



The bisphenol mold epoxy resin expressed with (R3 and R4 may be the same, or may differ, are a hydrogen atom, a methyl group, an ethyl group, or a phenyl group, and n is zero or more integers) (B), The polyol resin to which make at least one sort chosen from the reactant (D) of polyhydric alcohol (C) and this polyhydric alcohol, and an acid anhydride and the compound (E) which has an epoxy group and at least one active hydrogen radical which reacts in intramolecular come to react is offered.

[0006] Moreover, this invention also offers the toner for electrophotography which uses the aforementioned polyol resin as a principal component as a toner which is excellent in low-temperature fixable one, offset-proof nature, and blocking resistance.

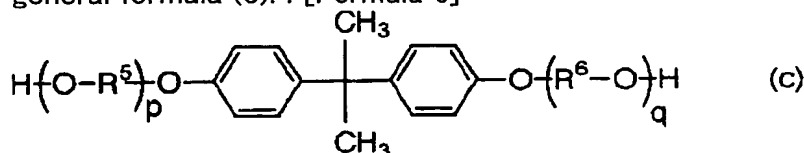
[0007] Hereafter, the polyol resin (henceforth "the resin of this invention") and the toner for electrophotography of this invention are explained to a detail.

[0008] The bisphenols (A) to which the resin of this invention is expressed with said general formula (a) The bisphenol mold epoxy resin expressed with said general formula (b) (B), At least one sort chosen from the reactant (D) of polyhydric alcohol (C) and this polyhydric alcohol, and an acid anhydride, With the compound (E) which has an epoxy group and at least one active hydrogen radical which reacts in intramolecular, use a cross linking agent (E) as the main raw material if needed further, these main raw materials are made to react, and it is obtained.

[0009] The bisphenols used as a main raw material (A) of the resin of this invention are expressed with said general formula (a). It sets to said general formula (a), and is R1. And R2 You may differ, even if the same, and they are a hydrogen atom, a methyl group, an ethyl group, or a phenyl group. As an example of these bisphenols (A), 2 and 2-screw (4-hydroxyphenyl) propane [common-name and bisphenol A], screw (4-hydroxyphenyl) methane [common-name and Bisphenol F], 1, and 1-screw (4-hydroxyphenyl) ethane [a common name and bisphenol A D], the 1-phenyl -1, 1-screw (4-hydroxyphenyl) methane, the 1-phenyl -1, 1-screw (4-hydroxyphenyl) ethane, etc. are mentioned. In this invention, these bisphenols may be used by the one-sort independent, and they may be used combining two or more sorts.

[0010] The bisphenol mold epoxy resin used as a main raw material (B) of the resin of this invention is expressed with said general formula (b). It sets at said ceremony (b) and is R3. And R4 You may differ, even if the same, and it is a hydrogen atom, a methyl group, an ethyl group, or a phenyl group, and n is zero or more integers. one so-called step manufactured from the bisphenols (A) expressed with said general formula (a), and epichlorohydrin as this bisphenol mold epoxy resin (B), for example -- law -- an epoxy resin or one step -- law -- [to which the two step method epoxy resin which is the polyaddition reaction product of an epoxy resin and bisphenols is mentioned -- Kakiuchi \*\*\*\*\* "new epoxy resin" (Shokodo) 30-page (Showa 60)]. In this invention, even if this bisphenol mold epoxy resin is independent one sort, it may be used in the combination of two or more sorts of mixture with which two or more kinds differ from number average molecular weight. When using two or more sorts of mixture with which two or more kinds differ from number average molecular weight, compared with the case where it uses by the one-sort independent, molecular weight distribution (Mw/Mn) become advantageous to improvement in a large next door and offset-proof nature. In this case, the number average molecular weight of a low molecular weight constituent is 300-3000, and it is desirable that the number average molecular weight of the amount component of macromolecules is 3000-10000.

In manufacture of the polyol resin of this invention, it is desirable from the viewpoint of the operability of feeding that a low molecular weight constituent is generally a principal component. [0011] In addition to the above (A) and (B), at least one sort chosen from the reactant (D) of polyhydric alcohol (C) and this polyhydric alcohol, and an acid anhydride is used for the resin of this invention as a main raw material. As polyhydric alcohol used as a main raw material (C), dihydric alcohol, such as aromatic series diol, aliphatic series diol, and alicycle group diol, trivalent or tetravalent alcohol, etc. can be mentioned. As aromatic series diol, it is the following general formula (c). : [Formula 6]



It comes out and the compound expressed is mentioned. It sets to a general formula (c) and is R5. And R6 You may differ, even if the same, and it is ethylene or a propylene radical, p and q are one or more integers, and p+q is 2-10. As an example of this aromatic series diol, it is a polyoxyethylene. - (2 0) -2, 2-screw (4-hydroxyphenyl) propane, Polyoxypropylene - (2 0) -2, 2-screw (4-hydroxyphenyl) propane, Polyoxypropylene - (1 2) -2, 2-screw (4-hydroxyphenyl) propane, Polyoxypropylene - (1 1) -2, 2-screw (4-hydroxyphenyl) propane, Polyoxypropylene - (2 2) - Polyoxyethylene - (2 0) -2, 2-screw (4-hydroxyphenyl) propane, Polyoxypropylene - (6) -2 and 2-screw (4-hydroxyphenyl) propane, polyoxypropylene - (3 3) -2, 2-screw (4-hydroxyphenyl) propane, etc. are mentioned. Moreover, in this invention, P-xylylene glycol and m-xylylene glycol can also be used as aromatic series diol.

[0012] As aliphatic series diol, ethylene glycol, a diethylene glycol, propylene glycol, triethylene glycol, tetramethylene glycol, pentamethylene glycol, neopentyl glycol, etc. are mentioned, for example. Moreover, as alicyclic diol, a dihydroxy methylcyclohexane, hydrogenation bisphenol A, etc. are mentioned, for example.

[0013] As trivalent or tetravalent alcohol, 1, 2, 3, 6-hexanetriol, 1, 4-sorbitan, a PENTA erythro toll, a TORIPENTA erythro toll, 1 and 2, 4-butane triol, trimethylolethane, trimethylol propane, 1 and 3, 5-trihydroxy methylbenzene, etc. are mentioned, for example.

[0014] Moreover, the reactant used as a main raw material (D) is a reactant of said polyhydric alcohol (C) and acid anhydride. As an acid anhydride used for a reaction with polyhydric alcohol (C) For example, phthalic anhydride, trimellitic anhydride, pyromellitic dianhydride, Ethylene glycol bis(trimellitate), glycerol tris trimellitate, A maleic anhydride, tetrahydro phthalic anhydride, methyl ten truck hydronalium phthalic anhydride, And methylene tetrahydro phthalic anhydride, methyl, and methylene tetrahydro phthalic anhydride, Methyl butenyl tetrahydro phthalic anhydride, dodecenyl succinyl oxide, Hexahydro phthalic anhydride, methyl hexahydro phthalic anhydride, a succinic anhydride, a methyl cyclohexene dicarboxylic acid anhydride, an alkyl styrene maleic anhydride copolymer, a chlorendic anhydride, and the Pori azelaic-acid anhydride can be mentioned.

[0015] The reaction time of 1 - 8 hours can usually perform the reaction of polyhydric alcohol and an acid anhydride at 80 degrees C - 150 degrees C under existence of a catalyst. The reaction of these polyhydric alcohol and an acid anhydride may be performed to coincidence with the polyaddition reaction in manufacture of the resin of after-mentioned this invention, and you may carry out before a polyaddition reaction. As for an acid anhydride acting as a cross linking agent, and gelation taking place depending on the case, for a certain reason, it is also desirable to carry out before a polyaddition reaction. As a catalyst used at this reaction, for example A sodium hydroxide, a potassium hydroxide, Alkali-metal alcoholates, such as alkali-metal hydroxides, such as a lithium hydroxide, and sodium methylate, Tertiary amine, such as N and N-dimethyl benzylamine, triethylamine, and a pyridine, Quarternary ammonium salt, such as tetramethyl ammonium chloride and benzyl triethyl ammonium chloride, Lewis acid, such as alkali-metal salts, such as organic phosphorous compounds, such as triphenyl phosphine and a triethyl phosphine, a lithium chloride, and a lithium bromide, a boron trifluoride, an aluminum

chloride, a tin tetrachloride, octylic acid tin, and zinc benzoate, etc. can be illustrated. The amount used is an amount usually preferably set to 5–500 ppm 1–1000 ppm to the amount of products. Moreover, it is even if it uses a solvent in this reaction. When using a solvent, ketones, such as aromatic hydrocarbon, such as toluene, a xylene, and ethylbenzene, methyl isobutyl ketone, and a methyl ethyl ketone, are desirable.

[0016] The compounds which have in intramolecular at least one the epoxy group and the active hydrogen radical which reacts used as a main raw material (E) of the resin of this invention are univalent phenols, secondary amine, and univalent carboxylic acids. As univalent phenols, a phenol, cresol, an isopropyl phenol, octyl phenol, nonyl phenol, a dodecyl phenol, a xylenol, P-cumyl phenol, the alpha-naphthol, the beta-naphthol, etc. are mentioned, for example. As secondary amine, ring content secondary amine, such as aliphatic series secondary amine, such as diethylamine, a dipropyl amine, dibutyl amine, dipentylamine, a didodecyl amine, a distearyl amine, diethanolamine, and a diaryl amine, N-methylaniline, N-methyl toluidine, N-methyl nitroaniline, a diphenylamine, a JITORIRU amine, and benzyl dimethylamine, etc. is mentioned, for example. As univalent carboxylic acids, ring content univalent carboxylic acids, such as aliphatic carboxylic acid, such as a propionic acid, butanoic acid, a caproic acid, a caprylic acid, pelargonic acid, and stearin acid, a benzoic acid, a toluic acid, alpha-naphthoic acid, beta-naphthoic acid, and a phenylacetic acid, can be mentioned, for example.

[0017] Furthermore, in manufacture of the resin of this invention, in case (E) is made to react with the above (A) and (B), and at least one sort chosen from (C) and (D), a cross linking agent (F) may be used if needed. As a cross linking agent (F), polyamine, such as aromatic series polyamine and aliphatic series polyamine, an acid anhydride, the phenolic compound more than trivalent, the epoxy resin more than trivalent, etc. are used. As polyamine, diethylenetriamine, TORIECHIREN triamine, iminobis propylamine, screw (hexamethylene) triamine, a trimethyl hexamethylenediamine, diethylamino propylamine, meta-xylylene diamine, a meta-phenylenediamine, diamino diphenylmethane, diamino diphenyl sulfone, etc. are mentioned, for example.

[0018] As an acid anhydride, for example Phthalic anhydride, trimellitic anhydride, pyromellitic dianhydride, Ethylene glycol bis(trimellitate), glycerol tris trimellitate, A maleic anhydride, tetrahydro phthalic anhydride, methyl cyclohexene-dicarboxylic anhydride, And methylene tetrahydro phthalic anhydride, methyl, and methylene tetrahydro phthalic anhydride, Methyl butenyl tetrahydro phthalic anhydride, dodecenyl succinyl oxide, Hexahydro phthalic anhydride, methyl hexahydro phthalic anhydride, a succinic anhydride, a methyl cyclohexene dicarboxylic acid anhydride, an alkyl styrene maleic anhydride copolymer, a chlorendic anhydride, the Pori azelaic-acid anhydride, etc. are mentioned. As a phenolic compound more than trivalent, for example Phenol novolak resin, Orthochromatic cresol novolak resin, 1 and 1, 1-tris (4-hydroxyphenyl) methane, 1, 1, 3-tris (2-methyl-4-hydroxy-5-tert-buthylphenyl) propane, 1, 1, 3-tris (2-methyl-4-hydroxy-5-tert-buthylphenyl) butane, 1-[alpha-methyl-alpha-(4-hydroxyphenyl) ethyl]-3-[alpha and alpha-screw (4-hydroxyphenyl) ethyl] benzene, 1-[alpha-methyl-alpha-(4-hydroxyphenyl) ethyl]-4-[alpha and alpha-screw (4-hydroxyphenyl) ethyl] benzene can be mentioned.

[0019] The epoxy resin more than trivalent is a glycidyl ghost obtained at the reaction of the phenolic compound more than trivalent or the alcoholic compound more than trivalent, and epihalohydrin. As a phenolic compound more than trivalent, for example Phenol novolak resin, orthochromatic cresol novolak resin, 1 and 1, and 1-tris (a 4-hydroxy phenylmethane →) 1, 1, 3-tris (2-methyl-4-hydroxy-5-tert-buthylphenyl) propane, 1, 1, 3-tris (2-methyl-4-hydroxy-5-tert-buthylphenyl) butane, 1-[alpha-methyl-alpha-(4-hydroxyphenyl) ethyl]-3-[alpha and alpha-screw (4-hydroxyphenyl) ethyl] benzene, 1-[alpha-methyl-alpha-(4-hydroxyphenyl) ethyl]-4-[alpha and alpha-screw (4-hydroxyphenyl) ethyl] benzene etc. is mentioned. As alcohol more than trivalent, they are 1, 2, 3, 6-hexane tetrol, 1, 4-sorbitan, pentaerythritol, dipentaerythritol, tripentaerythritol, 1 and 2, 4-butane triol, glycerol, isobutane triol, and 2-methyl, for example. - 1, 2, 4-butane triol, trimethylolethane, trimethylol propane, 1 and 3, 5-trihydroxy methylbenzene, etc. are mentioned.

[0020] Manufacture of the resin of this invention can be performed to said main raw material (A)



and (B), at least one sort chosen as a row from a raw material (C) and (D), the compound (E) which has an epoxy group and at least one active hydrogen radical which reacts in intramolecular, and a pan by carrying out the polyaddition reaction of the cross linking agent (F) if needed. As for the operating rate of each raw material, in this reaction, it is desirable to satisfy following formula (1) – (8).

A: Weight N5 of bisphenol A: The active hydrogen equivalent B1 of a bisphenol : Weight NB1 of a low-molecular-weight bisphenol mold epoxy resin : weight-per-epoxy-equivalent B-2 of a low-molecular-weight bisphenol mold epoxy resin : Weight-per-epoxy-equivalent C of the amount bisphenol mold epoxy resin of weight NB2: giant molecules of the amount bisphenol mold epoxy resin of giant molecules : [ The weight NC of polyhydric alcohol ] : Polyhydric-alcohol active hydrogen equivalent D: The amount ND of the acid anhydride with which a reaction with polyhydric alcohol is presented : Molecular weight E of an acid anhydride : amount NE of the compound which has an epoxy group and one active hydrogen which reacts in intramolecular : Molecular weight F of the compound which has an epoxy group and one active hydrogen which reacts in intramolecular: Weight NF of a cross linking agent : The active hydrogen equivalent of a cross linking agent, weight per epoxy equivalent (in the case of an acid anhydride, it is molecular weight)

[0021]

[Equation 2]

$$10000 \geq \frac{2(A_1 + B_1 + B_2 + C + D + E + F)}{E/N_E + |E/N_E + A/N_A + C/N_C + F/N_F - B_1/N_{B_1} - B_2/N_{B_2}|} \geq 1000 \quad (1)$$

(1) は製造しようとする樹脂の理論分子量を表す。

$$1.2 \geq \frac{B_1/N_{B_1} + B_2/N_{B_2}}{E/N_E + A/N_A + C/N_C + F/N_F} \geq 0.85 \quad (2)$$

(2) はエポキシ基当量数と活性水素基当量数の比を表す。

$$0.4 \geq \frac{B_2}{A_1 + B_1 + B_2 + C + D + E + F} \geq 0 \quad (3)$$

(3) は全原料中の高分子量エポキシ樹脂の割合を表す。

$$0.4 \geq \frac{C + D}{A_1 + B_1 + B_2 + C + D + E + F} \geq 0.03 \quad (4)$$

(4) は全原料中の多価アルコールまたは多価アルコールと酸無水物との反応物の割合を表す。

$$D = N_D \times C/N_C \quad \text{または} \quad D = 0 \quad (5)$$

(5) は多価アルコールと酸無水物の量比を表す。D = 0 は多価アルコールのみで反応する場合を表す。

$$0.15 \geq \frac{F}{A_1 + B_1 + B_2 + C + D + E + F} \geq 0.001 \quad (6)$$

(6) は全原料中の架橋剤の割合を表す。

但し架橋剤が3官能以上のエポキシ樹脂の場合は(1)および(2)式は(7)および(8)式となる。

$$10000 \geq \frac{2(A_1 + B_1 + B_2 + C + D + E + F)}{E/N_E + |E/N_E + A/N_A + C/N_C + F/N_F - B_1/N_{B_1} - B_2/N_{B_2}|} \geq 1000 \quad (7)$$

$$1.2 \geq \frac{B_1/N_{B_1} + B_2/N_{B_2} + F/N_F}{E/N_E + A/N_A + D/N_D} \geq 0.85 \quad (8)$$

Here, chain extension means being incorporated inside the principal chain of polyol resin, and the chain closure means being incorporated by the end of a principal chain. Moreover, a low-molecular-weight bisphenol mold epoxy resin means the epoxy resin of mean molecular weights 300-3000, and the amount bisphenol mold epoxy resin of giant molecules means the epoxy resin of mean molecular weights 3000-10000. Moreover, the weight per epoxy equivalent of an epoxy resin serves as the abbreviation half of the average molecular weight of an epoxy resin.

[0022] In manufacture of the resin of this invention, this polyaddition reaction is usually performed using a catalyst. As a catalyst used, for example A sodium hydroxide, a potassium hydroxide, Alkali-metal alcoholates, such as alkali-metal hydroxides, such as a lithium hydroxide, and sodium methylate, Tertiary amine, such as N and N-dimethyl benzylamine, triethylamine, and a pyridine, Quarternary ammonium salt, such as tetramethyl ammonium chloride and benzyl triethyl ammonium chloride, Lewis acid, such as alkali-metal salts, such as organic phosphorous compounds, such as triphenyl phosphine and a triethyl phosphine, a lithium chloride, and a lithium

bromide, a boron trifluoride, an aluminum chloride, and a tin etc. tetrachloride, etc. can be illustrated. In manufacture of the resin of this invention, when using a catalyst, the amount used is an amount usually preferably set to 5–500 ppm 1–1000 ppm to the amount of products.

[0023] In the polyaddition reaction in manufacture of the resin of this invention, it is also possible to use a solvent together. As a suitable solvent, aprotic polar solvents, such as ether [, such as ketones, such as aromatic compounds, such as a xylene and toluene, 2-butanone, methyl isobutyl ketone, and a cyclohexanone, ethylene glycol dibutyl ether, diethylene-glycol wood ether, a tetrahydrofuran, dioxane and an anisole, ], N, and N-dimethyl formamide, dimethyl sulfoxide, and 1-methyl-2-pyrrolidinone, can be illustrated. Even if these solvents are independent one sort, they can also mix and use two or more sorts. the case where a solvent is used -- the amount used -- usually -- 1- of the weight of a brewing raw material -- it is 5 - 50% of the weight of the amount which becomes comparatively preferably 100% of the weight.

[0024] Although the reaction temperature in this polyaddition reaction is based also on the amount of catalysts, the range of it is usually 120–180 degrees C. Moreover, generally, although a reaction can be pursued by measuring the number average molecular weight by weight per epoxy equivalent, the amount of phenolic hydroxyl groups, softening temperature, and GPC, it makes the time of an epoxy group disappearing substantially, at i.e., the time of becoming more than 20000 (g/Eq) as weight per epoxy equivalent, a reaction terminal point by this invention.

[0025] Thus, the thing of the range of 1000–10000 is desirable especially desirable, and the number average molecular weight ( $M_n$ ) of the resin of this invention obtained is usually the thing of the range of 2500–5000. As for the ratio ( $M_w/M_n$ ) of weight average molecular weight ( $M_w$ ) and number average molecular weight, what is 5–50 is desirable, and what is 10–35 is especially desirable. Moreover, softening temperature's 85–150-degree C thing is desirable, and what is 100–135 degrees C is especially desirable. Furthermore, a 50 degrees C - 90 degrees C thing is desirable, it is the point of reservation of low-temperature fixable one, offset-proof nature, and blocking resistance which is 55–70 degrees C, and, as for  $T_g$ , it is especially desirable. Moreover, the resin of this invention usually has the hydroxyl value of 120 - 200 KOHmg/g preferably 100 to 200 KOHmg/g.

[0026] Moreover, this invention offers the toner for electrophotography (henceforth "the toner of this invention") which uses said polyol resin as a principal component. The toner of this invention uses said polyol resin as a principal component, and contains various components, such as the coloring agent and the magnetic powder which are blended with this kind of toner for electrophotography, and binding resin, if needed.

[0027] The coloring agent regularly used by this kind of toner for electrophotography is sufficient as the coloring agent blended with the toner of this invention, and it is suitably chosen according to a desired color, compatibility with binding resin, etc., and is not restricted especially. For example, when preparing the black toner for electrophotography, a well-known black coloring agent can be used conventionally. As an example of a black coloring agent, pigments, such as carbon black and graft-ized carbon black which carried out the chemical treatment of the front face, can be mentioned. When preparing toners for electrophotography other than black, for example, yellow, a Magenta, or the toner for electrophotography of cyanogen in three primary colors, a well-known coloring agent can be used conventionally, respectively, and it is not restricted especially. For example, chromium yellow, quinoline yellow, etc. are mentioned as a coloring agent used when preparing the developer toner for electrophotography of yellow. Moreover, for example, E. I. du Pont de Nemours oil red, a rose bengal, etc. are mentioned as a coloring agent used when preparing the toner for electrophotography of a Magenta. Furthermore, the aniline bule, methylene-blue chloride, and a copper phthalocyanine blue are mentioned as a coloring agent used when preparing the developer toner for electrophotography of cyanogen.

[0028] The loadings of the coloring agent in the toner of this invention are an amount which usually becomes about 1 - 10 % of the weight preferably about 0.01 to 20% of the weight to the whole quantity of a toner. Moreover, magnetic powder is blended when using the toner of this invention as a magnetic toner which is 1 component system developer. As magnetic powder used, what consists of metals, such as ferrous oxide, such as a ferrite and magnetite, iron, cobalt, and nickel, is mentioned, for example, and these may be independent one sort or may be

used combining two or more sorts. Moreover, as for this magnetic powder, it is desirable that it is impalpable powder with a particle size of 1 micrometer or less. the case where it is the magnetic toner with which the toner of this invention contains magnetic powder -- the blending ratio of coal -- usually -- the binding resin 100 weight section -- receiving -- 30 - 300 weight section extent -- the 50 - 200 weight section comes out comparatively preferably.

[0029] Furthermore, the toner of this invention can blend various kinds of compounding agents regularly used by the conventional toner for electrophotography if needed in addition to the aforementioned binding resin, a coloring agent, or magnetic powder. For example, the styrene acrylic resin regularly used as binding resin, polyester resin, an epoxy resin, etc. can be blended. Moreover, flow improvers, such as release agents, such as an electric charge regulator, a plasticizer, low molecular weight polypropylene, low molecular weight polyethylene, paraffin wax, an amide wax, and a silicone oil, and a silica, etc. can also be blended if needed.

[0030] Use is usually preferably presented with the toner of this invention with the gestalt of a 5-15-micrometer particle the mean particle diameter of 3-20 micrometers. When considering as the pigment as binding resin and a coloring agent or a color, and the magnetic toner that is 1 component system developer, the toner of this invention carries out melting mixing using heating mixers, such as a heating roller, a kneader, and an extruder, after mixing an electric charge regulator, other additives, etc. enough with mixers, such as a Henschel mixer and a ball mill, magnetic powder and if needed further. Next, it can manufacture by performing grinding and a classification after cooling solidification using a jet mill etc.

[0031]

[Example] Hereafter, this invention is not limited by these examples although the example and the example of a comparison of this invention explain this invention more concretely. In addition, the weight per epoxy equivalent in an example and the example of a comparison, the number average molecular weight ( $M_n$ ) by GPC and weight average molecular weight ( $M_w$ ), a glass transition point, softening temperature, fixable, and blocking resistance were measured or evaluated according to the following approach.

[0032] 1) Add dioxane 25ml and make it dissolve, after weighing precisely the weight-per-epoxy-equivalent resin samples 0.2-5g and putting into a 200ml Erlenmeyer flask. 25ml (dioxane solvent) of solution of hydrochloric acid of 1/5 convention is added and sealed, and it puts for 30 minutes after mixing enough. Next, after adding 50ml (1:1 capacity factors) of toluene-ethanol mixed solutions, it titrates in a 1-/decanormal sodium-hydroxide water solution by using cresol red as an indicator. Based on a titration result, weight per epoxy equivalent (g/Eq) is calculated according to the following formula.

Weight-per-epoxy-equivalent (g/Eq) =  $1000 \times W / [(B-S) \times N \times F]$

W: The amount of sampling (g)

B: The amount of the sodium-hydroxide water solution which the blank test took (ml)

S: The amount of the convention sodium-hydroxide water solution which the trial of a sample took (ml)

N: Normality F of a sodium-hydroxide water solution : the potency of a sodium-hydroxide water solution [0033] 2) 80mg of measurement resin samples of the number average molecular weight ( $M_n$ ) by GPC and weight average molecular weight ( $M_w$ ) is dissolved in THF 10ml, prepare a sample solution, pour 100micro of this sample solution I into a column, and measure the holding time on condition that the following. Moreover, using the polystyrene of mean-molecular-weight known as the standard substance, the holding time was measured and the number average molecular weight of a resin sample was calculated by polystyrene conversion from the calibration curve created beforehand.

- Column : Guard column +GLR400M+GLR400M+ GLR400 (all Hitachi, Ltd. make)

- Column temperature : 40 degrees C - mobile phase (flow rate): THF (1 ml/min)

- Peak detection method : UV (254nm)

[0034] 3) Glass transition temperature ( $T_g$ ); it measured on the following conditions using the following differential scan mold calorimeter.

- Differential scanning calorimeter : SEIKO1DSC100 SEIKO1SSC5040 (Disk Station) - Measuring condition: Temperature requirement: 25-150 degrees C Programming rate: 10 degrees C / min

Sampling time: 0.5sec The amount of samples: 10mg [0035] 4) Softening temperature; softening point apparatus (the product made from METORA, FP90) was used, and the softening temperature of a sample was measured with the programming rate of 1 degree C / min.

5) the purification chloroform from which Resin 1.5–2.0g was weighed precisely and put into the (Measurement a) 25ml measuring flask of a hydroxyl value, and ethanol and water were removed by molecular-sieve 4A -- in addition, it was made to dissolve After dissolving resin completely, purification chloroform was added, the scalpel rise was carried out at the 25ml marked line, and the sample solution was prepared.

(b) Purification chloroform was considered for the sample solution as contrast for the KBr liquid cel (thickness: 0.2mm), and the absorption spectrum of the wave number field of 4000cm<sup>-1</sup>–3000cm<sup>-1</sup> was measured.

[0036] (c) Absorbance T1 of two absorption peaks which appeared And T2 It asked for the absorbance used as the base as criteria (zero). Next, T1+T2 From the calibration curve beforehand created from the value, it asked for hydroxyl-group concentration (eq/l), and the hydroxyl value was converted according to the following type.

Hydroxyl value (KOHmg/g) = (hydroxyl-group concentration / 4) thickness amendment of x56.1xF / [sample weight (g)] x100 F:KBr cel F=L1/L2L1 : Thickness of the cel of calibration-curve creation time (mm)

L2 : Thickness of the cel used at the time of measurement (mm)

[0037] After extracting 0.1, 0.2, 0.3, 0.4, and 0.5 and 0.6g for the purification diethylene glycol which dehydrated by molecular-sieve 4A in (Creation a) 6 \*\* 25ml flask of a calibration curve, respectively, the scalpel rise was carried out under purification chloroform at the marked line, and six sorts of standard solutions were prepared. These standard solutions are the standard solutions of the hydroxyl equivalent of 0.075, 0.151, 0.226, 0.301, 0.376, and 0.452 eq/l, respectively.

(b) Measure the absorption spectrum in the wave number field of 4000–3000cm<sup>-1</sup> about these standard solutions using a KBr liquid cel (thickness: 0.2mm). Absorbance T1 of two appearing absorption peaks And T2 It asks for the absorbance used as the base as criteria (zero), and is T1+T2. A value and the relation of a hydroxyl equivalent are plotted and it considers as a calibration curve.

6) Using the copy testing machine converted possible [ modification of the skin temperature of the heat roller for fixing of the electrophotography copying machine (Fuji Xerox 3500) by fixing trial Fuji Xerox ], the skin temperature of the heat roller for fixing was changed in 100–200 degrees C, and the copy by the above-mentioned developer was performed. Concentration change of the copy image when rubbing with the rubber of the copy image obtained was observed visually. The skin temperature of the heat roller for fixing was raised by 5-degree-C unit from 110 degrees C, and temperature when the rate of fixing exceeds 85% was made into the minimum fixing temperature. It examined by furthermore having raised temperature and temperature at which this toner began to adhere to a heat roller was made into offset initiation temperature.

[0038] 7) the inside of the glass sample bottle of 70ml of blocking resistance -- toner 10g -- putting in -- the constant temperature of 60 degrees C and 35% of relative humidity -- 3h was left in the constant humidity chamber. It cooled to the room temperature after that, whenever [ condensation ] was observed, and the following criteria estimated.

A: E from which a toner will fall if B:sample bottle to which a toner falls only by making a sample bottle reverse is made reverse, D:sample bottle to which a toner falls will be made reverse if C:sample bottle to which a toner falls is made reverse and is lightly struck only by shaking lightly, and a strong vibration is given : even if it makes a sample bottle reverse and gives a strong vibration, a toner does not fall. [0039] (Example 1) It is polyoxypropylene to capacity the separable flask of 500ml equipped with stirring equipment, a thermometer, a nitrogen inlet, and reflux tubing. – (1 1) –2 and 2-screw (4-hydroxyphenyl) propane (Mitsui Toatsu Chemicals, Inc. make, KB-280, OH \*\*:291 KOHmg/g) 33.9g, 26.1g [ of phthalic anhydride ], and xylene 15g was taught, and it stirred at 80 degree C of inside \*\* until the system became homogeneity. Next, the temperature up was carried out and it was made to react to 130 degrees C after adding benzyl

dimethylamine (BDMA) 30mg as a catalyst for 4 hours.

[0040] 41.3g of bisphenol A, 127.6g (Mitsui petrochemical company make, EPO MIKKU R140P, weight-per-epoxy-equivalent 188 g/eq) of the bisphenol A mold liquefied epoxy resins, 48g (Mitsui petrochemical company make, EPO MIKKU R309, weight-per-epoxy-equivalent 2750 g/eq) of the bisphenol A mold solid epoxy resins, 19.7g of benzoic acids, and 3.5g of stearin acid were prepared after cooling a reaction mixture at 50 degrees C or less, and 0.12g of tetramethyl ammonium chloride 50% water solutions was added at 80 degrees C. Reflux tubing was replaced with vacuum distillation equipment after the 1-hour reaction at 160 degrees C, and a xylene and water were gradually distilled off for whenever [ reduced pressure ] with slight height. Whenever [ reduced pressure ] amounted to 1333Pa (10mmHg) 1 hour after. After stirring for further 1 hour, the pressure in the system of reaction was returned to ordinary pressure, and stirring was continued for 7 hours. After having sampled the generated polyol resin at this time, measuring weight per epoxy equivalent and checking that weight per epoxy equivalent is 20000 or more, the generated polyol resin was extracted from the flask.

[0041] The softening temperature of the obtained polyol resin was [ 22 and the hydroxyl value of the ratio (Mw/Mn) of 124 degrees C, glass-transition-temperature:59 degree C, (number-average-molecular-weight Mn):3400, weight-average-molecular-weight (Mw):75000, weight average molecular weight (Mw), and number average molecular weight (Mn) ] 158 (KOHmg/g). Hereafter, this polyol resin is called (P-1). Here, it was checked that it is what is calculated with 0 by 0.20 and (6) formula, and is satisfied with 0.98 and (3) type about each preparation raw material of a \*\* (1) - (6) type at 3200 and (2) ceremony to (1) type with 0.16 and (4) type when the value of the aforementioned (1) - (6) type is calculated.

[0042] (Example 2) In the example 1, the amount of the raw material used was reacted like the example 1 except having changed 40.5g and a benzoic acid into 19.7g, and having changed [ bisphenol A / 46.1g and the bisphenol A mold liquefied epoxy resin ] stearin acid into 0g for 133.7g and the bisphenol A mold solid epoxy resin (weight per epoxy equivalent = 2640g/eq), and polyol resin was manufactured.

[0043] The softening temperature of the obtained polyol resin was [ 16.4 and the hydroxyl value of the ratio (Mw/Mn) of 121 degrees C, glass-transition-temperature:60 degree C, (number-average-molecular-weight Mn):3350, weight-average-molecular-weight (Mw):54800, weight average molecular weight (Mw), and number average molecular weight (Mn) ] 159 (KOHmg/g). Hereafter, this polyol resin is called (P-2). Here, it was checked that it is what is calculated with 0 by 0.20 and (6) formula, and is satisfied with 0.98 and (3) type about each preparation raw material of a \*\* (1) - (6) type at 3400 and (2) ceremony to (1) type with 0.135 and (4) types when the value of the aforementioned (1) - (6) type is calculated.

[0044] (Example 3) In the example 1, 0g, a benzoic acid, and stearin acid were changed [ the amount of the raw material used / bisphenol A / 51g and the bisphenol A mold liquefied epoxy resin ] into p-cumyl phenol 31.9g for 150.5g and the bisphenol A mold solid epoxy resin, except having added 6.6g of phthalic anhydride, it reacted like the example 1 and polyol resin was manufactured.

[0045] The softening temperature of the obtained polyol resin was [ 17.3 and the hydroxyl value of the ratio (Mw/Mn) of 123 degrees C, glass-transition-temperature:63 degree C, (number-average-molecular-weight Mn):4100, weight-average-molecular-weight (Mw):71000, weight average molecular weight (Mw), and number average molecular weight (Mn) ] 141 (KOHmg/g). Hereafter, this polyol resin is called (P-3). Here, it was checked that it is what is calculated with 0.022 by 0.20 and (6) formula, and is satisfied with 0.98 and (3) type about each preparation raw material of a \*\* (1) - (6) type at 3600 and (2) ceremony to (1) type with 0 and (4) types when the value of the aforementioned (1) - (6) type is calculated.

[0046] (Example 4) Set in the example 1. Polyoxypropylene (1 1) -2 and 2-screw (4-hydroxyphenyl) propane for the amount of the raw material used 17.0g, 48.8g and the bisphenol A mold liquefied epoxy resin for 13g and bisphenol A 150.8g, [ phthalic anhydride ] The benzoic acid was changed into 29.9g, 0g and the bisphenol A mold solid epoxy resin (weight per epoxy equivalent = 2640g/eq) were changed into 30g for stearin acid, except having added 10.5g of phthalic anhydride further, it reacted like the example 1 and polyol resin was manufactured.

[0047] The softening temperature of the obtained polyol resin was [ 20.6 and the hydroxyl value of the ratio (Mw/Mn) of 125 degrees C, glass-transition-temperature:60 degree C, (number-average-molecular-weight Mn):2500, weight-average-molecular-weight (Mw):59300, weight average molecular weight (Mw), and number average molecular weight (Mn) ] 156 (KOHmg/g). Hereafter, this polyol resin is called (P-4). Here, it was checked that it is what is calculated with 0.035 by 0.10 and (6) formula, and is satisfied with 0.98 and (3) type about each preparation raw material of a \*\* (1) - (6) type at 2300 and (2) ceremony to (1) type with 0.10 and (4) type when the value of the aforementioned (1) - (6) type is calculated.

[0048] (Example 5) Churning equipment, a thermometer, a nitrogen inlet, a distillation cooling pipe, and a receiver a separable flask with a capacity of 500ml which it had -- the bisphenol A mold liquefied epoxy resin (Mitsui petrochemical company make --) EPO MIKKU R140P, weight-per-epoxy-equivalent:188 (g/eq) 139.0g, 30.0g (Mitsui petrochemical company make, EPO MIKKU R309, weight per epoxy equivalent: 2640 (g/eq)) of bisphenol A mold solid epoxy resins, 39.6g of bisphenol A, polyoxypropylene (1 1) -2, and 2-screw (4-hydroxyphenyl) propane (the Mitsui Toatsu Chemicals, Inc. make --) KB-280, OH\*\*:291KOHmg/g15.0g, P-cumyl phenol 67.4g, 9.0g [ of phthalic anhydride ], and xylene 30g was taught, the temperature up was started under nitrogen-gas-atmosphere mind, and it was made to dissolve in homogeneity at 80 degree C of inside \*\*. Subsequently, 1.0g of 10% water solutions of sodium hydroxides was added as a reaction catalyst. Furthermore the temperature up was carried out, and the vacuum concentration of a xylene was started and it decompressed to 1333Pa over about 0.5 hours in the place where inside \*\* reached 180 degrees C. The pressure of the system of reaction is returned to ordinary pressure, and it was made to react under reduced pressure for 7 hours, after stirring for 1 hour, maintaining reaction temperature at 180 degrees C further. When the amount of survival of an epoxy group was measured at this time, weight per epoxy equivalent was more than 20000 (g/Eq). Since it checked that the epoxy group had disappeared substantially, the polyol resin of the generated melting condition was extracted from the flask.

[0049] The softening temperature of the obtained polyol resin was [ 17.6 and the hydroxyl value of the ratio (Mw/Mn) of 116 degrees C, glass-transition-temperature:59 degree C, (number-average-molecular-weight Mn):2600, weight-average-molecular-weight (Mw):45800, weight average molecular weight (Mw), and number average molecular weight (Mn) ] 146 (KOHmg/g). Hereafter, this polyol resin is called (P-5). Here, it was checked that it is what is calculated with 0.03 by 0.05 and (6) formula, and is satisfied with 0.98 and (3) type about each preparation raw material of a \*\* (1) - (6) type at 1800 and (2) ceremony to (1) type with 0.1 and (4) type when the value of the aforementioned (1) - (6) type is calculated.

[0050] (Example 1 of a comparison) Dimethyl terephthalate 450.1g, dimethyl phthalate 13.9g, propylene glycol 400g, and 0.18g of oxalic acid tin were taught to the separable flask with an equipped with churning equipment, the thermometer, the nitrogen inlet, the distillation cooling pipe, and the receiver capacity of 1l., and the temperature up was carried out to 170 degrees C. After distilling off of a methanol was started, the temperature up was carried out gradually, methanol 160g was distilled off at 200 degrees C, and transformer esterification was completed. Next, the macromolecule quantification reaction was continued for 5 hours, having kept the temperature in the system of reaction at 210 degrees C, having kept the pressure at 1333Pa, and distilling off propylene glycol. Furthermore, the reaction was performed after adding 17.2g of phthalic anhydride for further 3 hours, and the generated resin was picked out from the flask. The softening temperatures of the obtained polyester resin were 121 degrees C, glass-transition-temperature:68 degree C, (number-average-molecular-weight Mn):3300, weight-average-molecular-weight (Mw):7800, and Mw/Mn:2.4.

[0051] (Example 6) Set in the example 1. It is polyoxypropylene about the amount of the raw material used. - (1 1) -2 and 2-screw (4-hydroxyphenyl) propane 45.2g, 155.3g and a biphenol A mold liquefied epoxy resin for 34.8g and bisphenol A 342.8g, [ phthalic anhydride ] Change the bisphenol A mold solid epoxy resin into 120g, and a benzoic acid is changed into 69.9g. Stearin acid was not used but polyol resin was further manufactured like the example 1 except having added 32.0g (the Mitsui Chemicals [ , Inc. ] make, TEKUMOA VG-3101, weight per epoxy equivalent: 210g/eq) of 3 organic-functions epoxy resins. The softening temperatures of the

obtained polyester resin were 120 degrees C, glass-transition-temperature:64 degree C, (number-average-molecular-weight Mn):2860, weight-average-molecular-weight (Mw):46600, Mw/Mn:16.3, and hydroxyl value:167 (KOHmg/g). Here, it was checked that it is what is calculated with 0.98 by 2600 and (8) formulas, and is satisfied with 0.10 and (6) type about each preparation raw material of a \*\* (3) - (8) type at 0.15 and (4) ceremony to (3) types with 0.04 and (7) type when the value of the aforementioned (3) - (8) type is calculated.

[0052] (Example 7) Melting kneading of 180g [ of polyol resin obtained in the example 1 ] (P-1) and carbon black (Mitsubishi Chemical make, MA-100) 12g, polypropylene wax (Mitsuhiro formation shrine make, the bis-call 660 P) 4g, and the SUPIRON black TRH(Hodogaya chemistry company make)4g was carried out with 2 rolls after mixing by the super mixer. The polyol resin powder which grinds the obtained mixture with a jet mill after cooling, classifies it with a dry type air-current classifier further, and consists of a particle with a mean particle diameter of 10 micrometers was obtained. Subsequently, the hydrophobic silica (the product made from Japanese Aerosil, R972) was mixed at a rate which becomes 0.4wt(s)% of the whole quantity, within the Henschel mixer, twice, it stirred for 30 seconds and the toner for electrophotography was obtained. Blocking resistance of this toner for electrophotography was evaluated. Moreover, obtained toner 5g for electrophotography and iron powder carrier (mean particle diameter: 60-100 micrometers) 95g were mixed to homogeneity, the developer was prepared, and the fixing trial was performed using the developer. A result is shown in Table 1.

[0053] (Examples 8-12) In each example, the toner for electrophotography was manufactured like the example 7 instead of polyol resin (P-1) except having used polyol resin P-2-7. Blocking resistance and fixable evaluation were performed about the obtained toner. A result is shown in Table 1.

[0054] (Example 2 of a comparison) Except having used the polyester resin compounded in the example 1 of a comparison instead of polyol resin (P-1), the toner was manufactured like the example 7 and it evaluated blocking resistance and fixable. A result is shown in Table 1.

[0055]

表 1

	実施例 7	実施例 8	実施例 9
耐ブロッキング性	A	A	A
定着試験			
最低定着温度(℃)	130	125	130
オフセット開始温度(℃)	190	185	185

	実施例 10	実施例 11	実施例 12	比較例 2
耐ブロッキング性	A	A	A	A
定着試験				
最低定着温度(℃)	135	125	130	135
オフセット開始温度(℃)	180	165	180	155

[0056]

[Effect of the Invention] Since the polyol resin of this invention is used as a principal component of the toner for electrophotography, it excels in the offset-proof nature in fixable and an elevated temperature in low temperature and it excels in blocking resistance further, a toner suitable as a developer for electrophotography which is not blocked even if saved for a long



period of time can be offered. Moreover, the offset-proof nature is fixable and an elevated temperature in low temperature, and since it excels in blocking resistance further, the toner for electrophotography of this invention is suitable as a toner for electrophotography.

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[Translation done.]